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Determination of trapping parameters of dosimetric thermoluminescent glow peak of lithium triborate (LiB_3O_5) activated by aluminum

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ABSTRACT

Lithium triborate (LBO) is a newly developed ideal nonlinear optical (NLO) crystal used in laser weapon, welder, radar, tracker, surgery, communication, etc. The effective atomic number ($Z_{eff} = 7.3$) makes it a tissue equivalent material and this encourages studies on its thermoluminescence (TL) properties for a radiation dosimetry. The previous studies have shown that Al-doped LiB_3O_5 is a promising thermoluminescent dosimetric (TLD) material for dosimetric purposes and continuous and systematic investigations to improve its quality to get ones suited for dosimeter applications are worthy. In the given study, the additive dose (AD), initial rise with partial cleaning (IR), variable heating rate (VHR), peak shape (PS), three-points method (TPM) and computerized glow deconvolution (CGCD) methods were used to determine the kinetic parameters, namely the order of kinetics (b), activation energy (E_a) and the frequency factor (s) associated with the dosimetric thermoluminescent glow peak (P3) of Al-doped LiB_3O_5 after different dose levels with β-irradiation.

1. Introduction

Lithium triborate, LiB_3O_5, is one of the most known lithium borates. It is a newly developed nonlinear optical (NLO) crystal. It offers the following advantages: extremely high damage threshold, large phase matching acceptance angle, very wide transparency range and chemical stability. So it is particularly useful for making doubler or tripler for lasers such as Nd: YAG lasers for which high power density, high stability and long time operation are required. It is an ideal nonlinear optical crystal used in laser weapon, welder, radar, tracker, surgery, communication, etc. [1].

The tissue equivalent absorption coefficient is one of the most important properties of the thermoluminescent dosimetric (TLD) materials in the field of medical physics. Although the thermoluminescence (TL) properties of lithium borate crystals are highly affected by the experimental conditions during the crystal growth, the TL studies of lithium borate compounds are of interest because of their near tissue equivalent absorption coefficient ($Z_{eff} = 7.3$), low cost and easy handling process. Therefore, it is particularly suited for applications in radiation dosimetry, especially radiation therapy and clinical applications. Therefore, the TL studies of lithium borate compounds were started in 1967 by the work of Schulman et al. [2] and then, detailed TL studies on various alkali and alkaline earth tetra borates, especially on the lithium and magnesium borate compounds, were started and are continuing [3–5]. Recently, Prokic reported that the sintered $Li_2B_4O_7$ doped with several impurities such as Cu, In; Cu, In, Ag; and Mg, Cu, P gives better dosimeter characteristics than others [1]. These materials have good tissue equivalence as TL dosimeters and they show sensitivity similar to that of TLD-100 (LiF:Mg,Ti). In addition, doped lithium borate crystals may be potential materials for neutron detection, due to the presence of Li and B. Because of the presence of the Li and B in the structure, efficient neutron capture is expected with high-energy deposits. Since lithium borate has a low effective atomic number and low material density, it will have low efficiency for gamma ray background detection.

The dosimetric characteristics of any TL material mainly depend on the sensitivity, energy response and the kinetic parameters quantitatively describing the trapping–emitting centers responsible for TL emission. Thus, a reliable dosimetric study of a thermoluminescent material should be based on a good knowledge of its kinetic parameters. For example, simultaneous estimation of dose rate and time elapsed since exposure are closely related to the position of the trapping levels within the band gap, and therefore it is necessary to have a good knowledge of these parameters. There are various methods for evaluating the trapping parameters (order of kinetics (b), activation energy (E_a) and the frequency factor (s)) from TL glow curves. When one of the glow peaks is highly isolated from the others, experimental methods such as initial rise, various heating rates and peak shape (PS) methods are suitable to determine them. Therefore, in the

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given study, additive dose (AD), initial rise with partial cleaning (IR), variable heating rate (VHR), peak shape, three-points method (TPM) and computerized glow deconvolution (CGCD) methods were used to determine the kinetic parameters namely the order of kinetics (b), activation energy (E_a) and frequency factor (s) associated with dosimetric thermoluminescent glow peak (P3) of Al-doped LiB_3O_5 after different dose levels with β-irradiation.

2. Experimental procedure

The sample used in this study was lithium triborate doped with 5 wt% Al ions. The details of sample preparation were given in the previously published studies [6–7]. In this study, 20 mg sample was used in each measurement. The samples were firstly annealed at 350±1 °C for 15 min prior to irradiation with a specially designed microprocessor-controlled electrical oven and then they are irradiated at room temperature with a newly calibrated ^{90}Sr–^{90}Y β-source (D≈0.04 Gy/s). The glow curves were obtained by using a Harshaw QS 3500 Manual-type TL reader interfaced to a PC where the TL signals were analyzed. Glow curve readout was carried out on a platinum planchet at a linear heating rate of 1 °C/s up to 400 °C, except for the heating rate experiments. In the variable heating-rate method, the heating rates were changed between 1 and 10 °C/s.

3. Results

Previously published studies have shown that determination of activation energy and frequency factor mainly depends on the prior knowledge of kinetic order and the exact number of glow peaks in the glow curve [7–9]. Therefore, to form an opinion about the number of glow peaks and kinetic orders of all individual glow peaks in the glow curve structure of Al-doped LiB_3O_5, the additive dose method was firstly utilized in the current study. The samples were irradiated at different doses between ≈0.04 and ≈114 Gy to check the dose-dependence effect on the peak positions. Some of the selected glow curves after different dose levels are shown in Fig. 1. The experimental observations have clearly shown that there were no significant changes in the peak temperature of glow peak of Al-doped LiB_3O_5 with increasing dose level (Fig. 1). As seen from this figure, the positions of peak temperature of P3 are within the experimental error ±2 °C for all the doses. This result clearly shows that the P3 and also all of the glow peaks of Al-doped LiB_3O_5 should have first-order kinetics.

The recorded glow curves after the additive dose experiments were also used to determine the kinetic parameters by the PS method. This method is based on the shape and full-width at half maximum (FWHM = T_2–T_1) of a single glow peak and the values of E_a were determined by the modified PS method of Chen [10]. According to this method, the kinetic order of a single peak is easily obtained by means of the geometric factor {$\mu_g = (T_2–T_m)/(T_2–T_1)$} and μ_g changes with the order of kinetics from ≈0.42 to ≈0.52, where these two limits correspond to first- and second-order kinetics, respectively. In addition to Chen's peak shape method the kinetic parameters have also been determined by using Gartia et al. [11] peak shape method, which requires the prior knowledge of the kinetics order. In the present case, the symmetry factor (μ_g) of the isolated glow peak 3 of Al-doped LiB_3O_5 has been found to be 0.42±0.01, which gives a kinetic order of about 1. The method uses any point of a peak (i.e., $x = I_m/2$, or $2I_m/3$, or $4I_m/5$ where I_m is the maximum peak intensity). According to this method, it is possible to calculate the activation

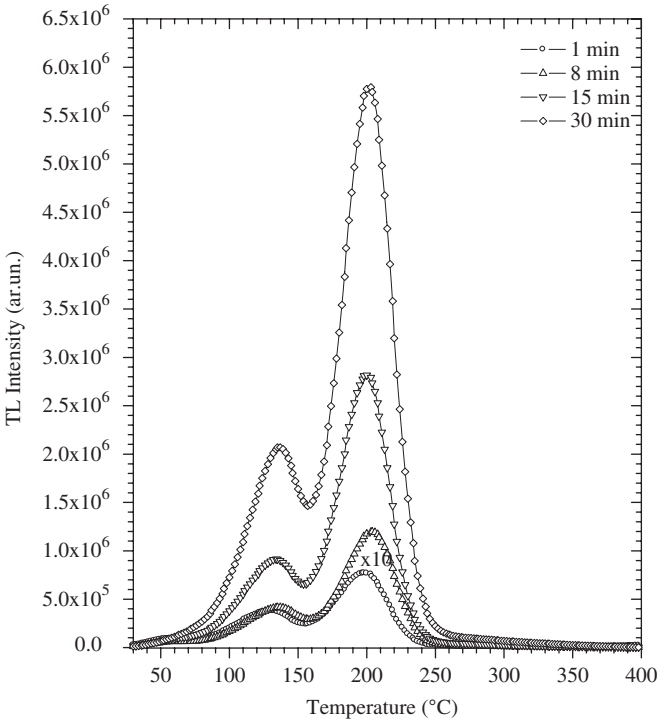

Fig. 1. The glow curve of Al-doped LiB_3O_5 measured after various radiation-exposed dose levels ($\beta = 1$ °C/s).

Table 1
Values of the activation energy E_a (eV) and frequency factor s (s^{-1}) of main dosimetric peak of Al-doped LiB_3O_5 determined by the modified PS method of Gartia et al. [11].

	1/2 ratio			2/3 ratio			4/5 ratio		
	E_τ	E_δ	E_ω	E_τ	E_δ	E_ω	E_τ	E_δ	E_ω
E_a (eV)	1.04	1.07	1.06	1.07	1.02	1.06	1.01	1.06	1.06
ln(s) (s^{-1})	22.41	23.28	23.05	23.30	22.18	23.06	21.88	23.06	23.05

It was assumed that $b \approx 1$ in Eq. (1).

energy as follows:

$$E_a = \frac{(C_0 + C_1 b + C_2 b^2) k T_m^2}{|T_x - T_y|} + (D_0 + D_1 b + D_2 b^2) k T_m \quad (1)$$

where k (eV K^{-1}) is Boltzmann's constant, $|T_x–T_y| = \tau,\delta,\omega$ and C_0, C_1, C_2, D_0, D_1 and D_2 are the coefficients found by using the method of least squares for different order of kinetics b in the range from 0.7 to 2.5 for different values of x [11]. Gartia et al. [11] claim that the E_a values obtained by using Eq. 1 for $x = 1/2$ gives more accurate results than Chen's peak shape equations. As a result, the trapping parameters of this peak calculated by this method are given in Table 1.

Recently, Rasheedy [12] has improved the three points analysis method for separating a composite TL glow curve into its individual components of glow peaks and to evaluate the trap parameters of these peaks. According to this method, the order of kinetics b is given by

$$b = \frac{T_y[T_x - T_z]\ln(y) - T_z[T_x - T_y]\ln(z)}{T_y[T_x - T_z]\ln[A_x/A_y] - T_z[T_x - T_y]\ln[A_x/A_z]} \quad (2)$$

where A_x, A_y and A_z are the areas under the glow peak from the temperatures T_x to T_f, T_y to T_f and T_z to T_f, respectively. The values of y and z are given by $y = (I_x/I_y)$ and $z = (I_x/I_z)$. The activation

energy E_a is given either by

$$E_a = \{\ln y - b\,ln[A_x/A_y]\}\left\{\frac{kT_xT_y}{T_x - T_y}\right\} \text{ or by} \quad (3)$$

$$E_a = \{\ln z - b\,\ln[A_x/A_z]\}\left\{\frac{kT_xT_z}{T_x - T_z}\right\} \quad (4)$$

Also, the frequency factor s in the case of first order is given by

$$s = (\beta E_a/kT_m^2)\,\exp(E_a/kT_m), \quad (5)$$

In the present study, the trapping parameters evaluated from the three-points method are the results of calculations from the maximum intensity at temperature ≈200 °C (P3) up to 10% of the maximum intensity. The average values of the trapping parameters associated with peak 3 are given by $b = 1.1$, $E_a = 1.02$ eV and $s = 4.279 \times 10^9\ s^{-1}$.

Another method that was used to determine the kinetic parameters in this study is the variable heating-rate method. This method is based on the shift position of the temperature (T_m) at the maximum point of intensity (I_m) to higher temperatures when the heating rate is increased. In the absence of a distribution of activation energies, a plotting of $\ln(T_m^2/\beta)$ against $1/(kT_m)$ should give a straight line of slope E_a/k and intercept $\ln(sk/E_a)$. The major advantage of this method is that the required data are to be taken at a peak maximum (I_m, T_m), which, in the case of a large peak surrounded by smaller satellites, can be reasonably accurately determined from the glow curve. For the variable heating-rate method, the three heating rates of 1, 3 and 5 °Cs^{-1} were applied. The measured and the normalized glow curves after these three heating rates are shown in Fig. 2. It is clearly seen from this figure that the peak temperatures of all glow peaks increase with increasing heating rate. As a result, the calculated kinetic parameters from the slopes and intercepts by the variable heating-rate method are given in Table 2.

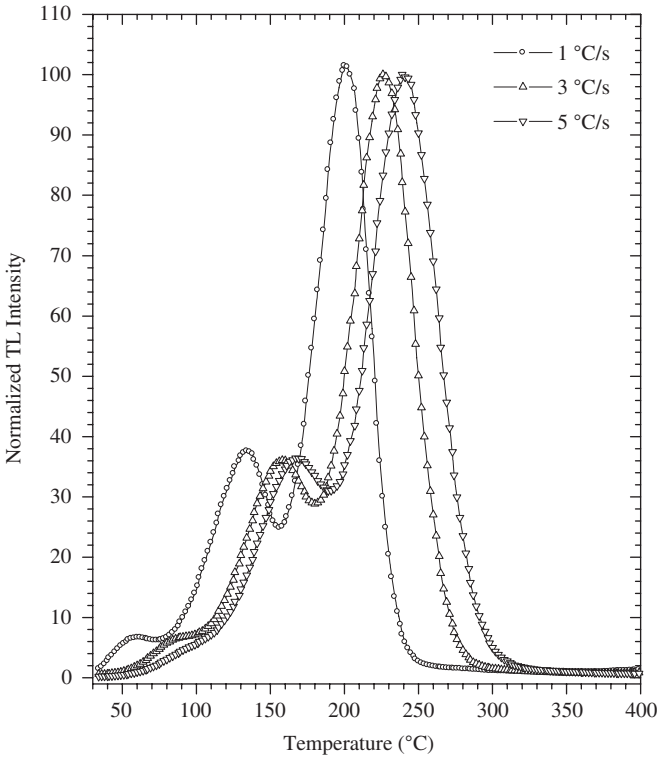

Fig. 2. Some of the selected and normalized glow curves of Al-doped LiB_3O_5 measured at various heating rates for 1, 3 and 5 °C/s. All glow curves were measured after β-irradiation of 12 Gy.

Table 2
Values of the activation energy E_a (eV) and frequency factor s (s^{-1}) of main dosimetric peak of Al-doped LiB_3O_5 determined by the Chen's PS, IR, VHR and TP methods.

	IR	VHR	Chen's PS			TP	CGCD
			E_τ	E_δ	E_ω		
E_a (eV)	1.26	1.10	0.99	0.98	1.0	1.02	0.98
$\ln(s)$ (s^{-1})	34.3	20.11	21.32	21.06	21.57	22.17	21

The kinetic parameters of main dosimetric peak 3 were also tested using the initial rise with partial cleaning method. A strong overlapping of TL peaks makes this method the most suitable procedure for the determination of number of glow peaks and their related kinetic parameters. Here, an irradiated sample is heated at a linear heating rate up to a temperature T_{stop} corresponding to a point on the low-temperature tail of the first peak. The sample is then cooled down quickly to room temperature and then re-heated at the same rate to record the entire remaining glow curve and the value of activation energy E_a is calculated. The process is repeated several times on the same annealed/irradiated sample at different T_{stop} values, and the two measurements were taken within each 10 °C region. According to this method, at the beginning of the TL glow peak, the concentration of trapped electrons n_0 changes by only a small amount with temperature and thus it can be regarded as constant, so that the first- and general-order TL equations are simplified as $I(T) \propto A\,\exp(-E_a/kT)$, where A is a constant and the TL intensity is independent of the kinetic order b. Therefore, a plot of $\ln(I)$ vs $1/T$ would yield a straight line with a slope of $-E_a/k$ and a y-intercept of $\ln(s/\beta)$, from which E_a and s can be readily calculated. This method can be used only in the initial region of the TL signal up to ~10% of its peak maximum (I_m). However, if the intensity at the beginning of each peak is very low and especially when the glow curve is composed of several glow peaks, the obtained values of E_a may not reflect the actual values. Therefore, in this case, the values of activation energy obtained by the repeated initial rise method often need corrections. Christodoulides [13] and Singh et al. [14] have proposed to use the high level of glow peaks to reduce the inaccuracies in E_a due to high levels of the used signal, which was also used in the present work. Another matter during the evaluation of activation energy E_a by initial rise method is the effect of thermal quenching. This effect leads to underestimations of the activation energies obtained by the IR method. Since the experimental glow curve shape is highly distributed by thermal quenching effect, it cannot give reliable information on the values of activation energy E_a.

However, the initial rise with partial cleaning method analyzes only the leading part of the glow peak and as such is yielding data appropriate to only that component of the TL signal comprising the full peak. Therefore, even if the IR method gives erroneous values of E_a when the thermal quenching is present in the material, it should be expected that the plot of E_a against T_{stop} still gives plateau regions with a gradual decrease at the end of each plateau after initial rise method even if the glow curve is the superposition of overlapping glow peaks. If a plot of E_a against T_{stop} shows a stepwise curve after the initial rise method, it allows one to estimate the number of peaks. Each plateau region in this plot indicates the existence of an individual glow peak. If a gradual rise of E_a exists at the end of the plateau region, it is an indication that the glow curve has overlapping glow peaks. Fig. 3 shows some of the selected glow curves after the T_m–T_{stop} procedure following the irradiation of samples to a dose level $D = 12$ Gy. As seen from this figure, the T_m of all glow peaks is continuously

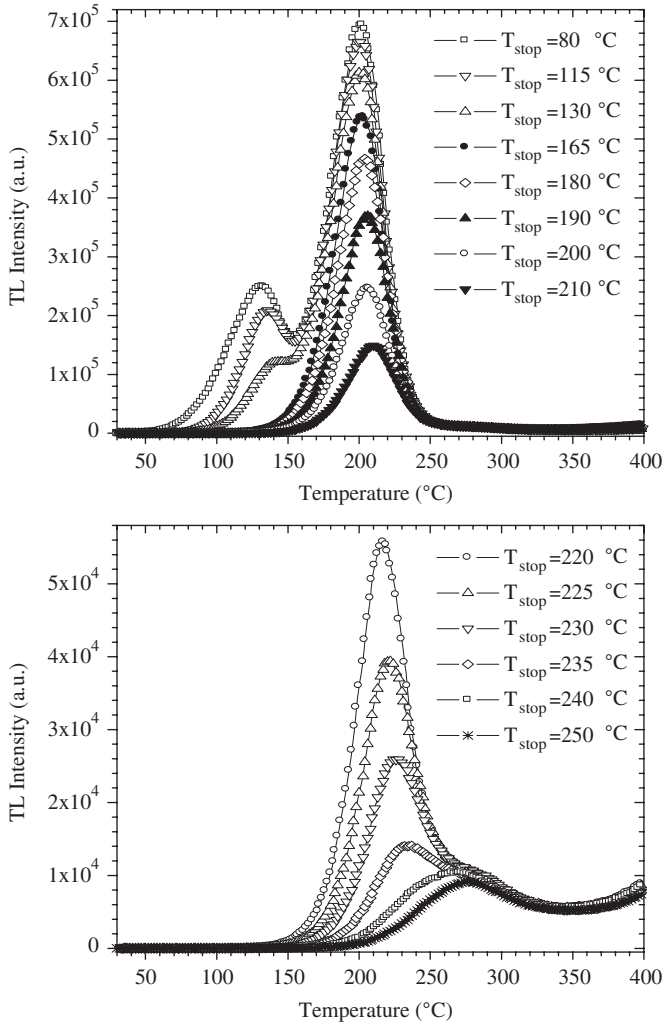

Fig. 3. Some of the selected glow curves of Al-doped LiB_3O_5 after different T_{stop} temperatures at a linear heating rate $\beta = 1\,^{\circ}C/s$. Dose levels are always adjusted to 12 Gy.

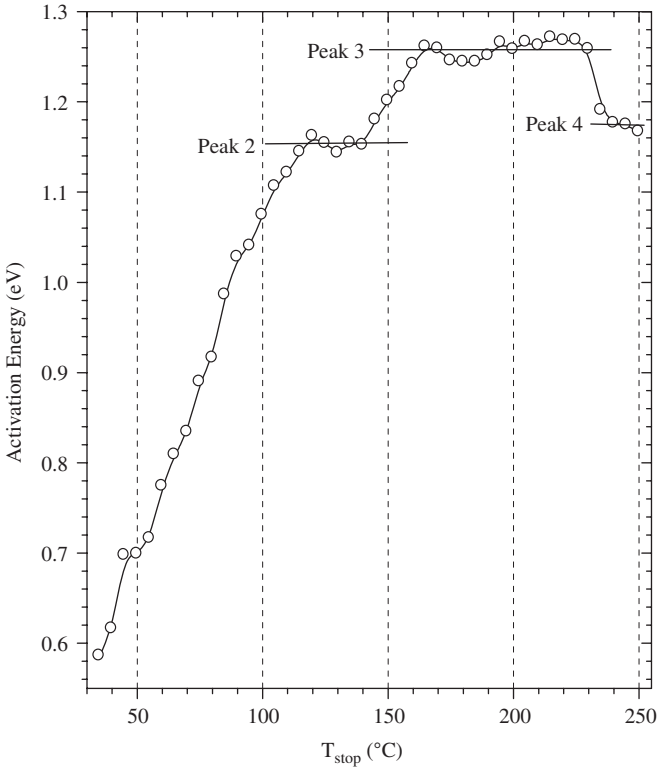

Fig. 4. Activation energy (E_a) resulting from the initial rise method with partial cleaning procedure.

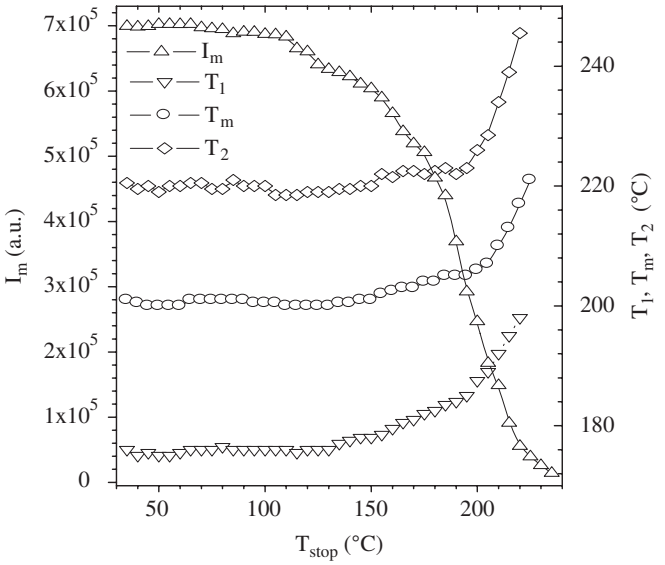

Fig. 5. T_1–T_{stop}, T_m–T_{stop}, T_2–T_{stop} and I_m–T_{stop} plots for the thermoluminescent dosimetric glow peak of Al-doped LiB_3O_5.

shifted to high-temperature side with increasing T_{stop}. The result of calculated activation energies is shown in Fig. 4. As shown from this figure, there are four plateau regions, so the IR studies have identified four peaks in aluminum-activated lithium triborate, designated P1–P4, in the temperature range ~50–300 °C. The first plateau region is around 60 °C. After the disappearance of peak 1 above $T_{stop} > 120\,^{\circ}C$, another plateau region was obtained. After the complete depletion of peak 2, another flat region between 160 and 240 °C becomes constant around 1.26 ± 0.02 eV, which corresponds to peak 3. At the end of this region, another flat region was again obtained above $T_{stop} > 240\,^{\circ}C$, which belongs to peak 4.

In this paper we have also examined the effect of T_{stop} on the T_1, T_2, T_m, μ_g and I_m of peak 3. Fig. 5 shows the changes in them as functions of T_{stop}. As seen from this figure the maximum peak intensity of peak 3 is constant up to $T_{stop} = 100\,^{\circ}C$. As T_{stop} increases I_m starts to decrease because T_{stop} reaches the maximum peak temperature of about 200 °C. In Fig. 6a it can be seen that the shape parameter μ_g is between 0.42 and 0.45 up to $T_{stop} = 120\,^{\circ}C$. Its value increases slowly with a small up–down change, until maximum peak temperature. Above $T_{stop} > 200\,^{\circ}C$ the shape parameter increases continuously reaching the value of about 0.6. Fig. 6b also shows the variation of activation energy E_a vs T_{stop} obtained by PS method. It can be concluded from this figure that E_a is constant at about 1.12 eV with a small change until $T_{stop} = 100\,^{\circ}C$, and then increases continuously, and reaches the value of 1.36 eV about its maximum peak temperature.

The glow curve of this sample was also analyzed by the CGCD method in our previous study [7]. This method has become very popular to obtain kinetic parameters for the last two decades [15–16]. The activation energy (E_a) and the frequency factor (s) for the main dosimetric peak of LiB_3O_5 were determined to be 0.98 ± 0.02 eV and $1.318 \times 10^9\ s^{-1}$, respectively.

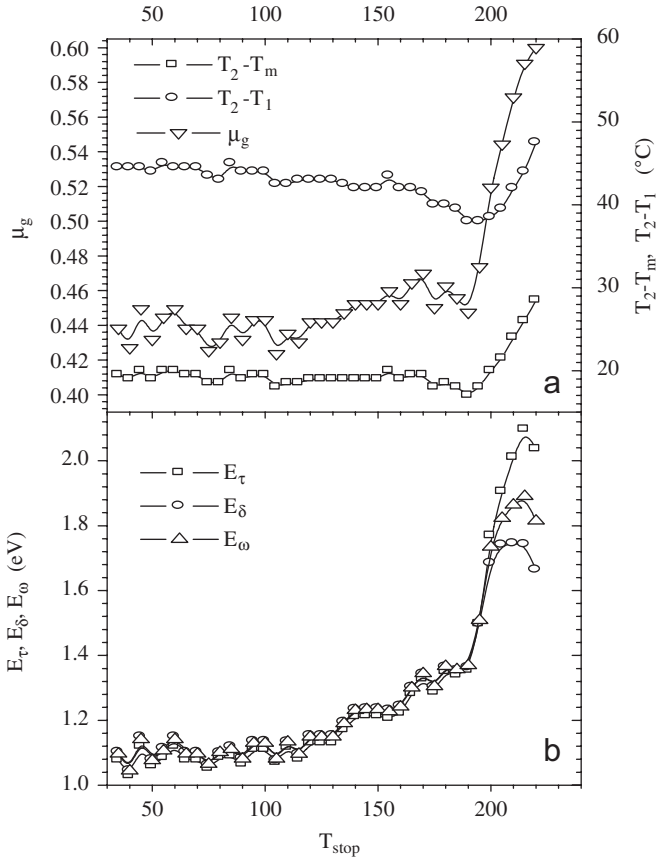

Fig. 6. (a) Geometric factor μ_g, T_2-T_1 and T_2-T_m as a result of T_{stop} determined from the T_m-T_{stop} procedure. (b) Activation energy (E_a) resulting from the peak shape method after the T_m-T_{stop} procedure.

4. Conclusion

The results in this paper indicate that the glow curve of Al-doped LiB_3O_5 after β-irradiation between 0.04 and ≈5 Gy in the temperature range from room temperature to 400 °C is the superposition of at least three glow peaks. On the other hand, when the dose level is increased above ≈5 Gy, a new peak (peak 4) starts to generate at the high-temperature side of the main dosimetric peak. Kinetic order (b), activation energy (E_a) and frequency factor (s) of the main dosimetric peak were calculated by applying different experimental methods. In order to determine the kinetic order from the glow curve, the AD method was used firstly and it indicates that all of the glow peaks have first-order kinetics. Also Chen's peak shape method showed that the symmetry factor $\{\mu_g = (T_2-T_m)/(T_2-T_1)\}$ of the isolated glow peak 3 of Al-doped LiB_3O_5 has been found to be 0.42 ± 1, which gives a kinetic order of about 1.05 ± 0.05. A similar result was also obtained by the CGCD method.

The values of the activation energy were calculated by using Gartia, Singh & Mazumdar's PS method for different x-values, the TP method developed by Rasheedy, the IR, VHR, CGCD and Chen's PS methods. The results are tabulated in Tables 1 and 2. As can be seen from these tables, the average values of the E_a values of P3 obtained by the TP, CGCD, VHR and PS methods of Chen and Gartia, Singh & Mazumdar give very close results. As seen, the value of the activation energy obtained by these methods is about 1.05 ± 0.05 eV. On the other hand, value of E_a obtained by the IR method gives slightly higher values as compared with those methods. One possible explanation for these differences is that the P3 does not originate from a discrete energy level and it is a distribution of traps. In reality, when the T_m-T_{stop} procedure was checked it is seen that the position of peak slightly shifts toward the high-temperature side with increasing T_{stop} (Fig. 5). This result indicates that it has a distribution of traps and a heat treatment after irradiation may cause a variation in the activation energies of this peak.

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